

# The characteristics of wet air oxidation of phenol over $\text{CuO}_x/\text{Al}_2\text{O}_3$ catalysts: Effect of copper loading

Sang-Kyung Kim, Kyoung-Hun Kim, Son-Ki Ihm \*

*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology,  
373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea*

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## Abstract

The nature of active copper species is well-known to vary with copper loading, i.e., isolated  $\text{Cu}^{2+}$  to bulk CuO. In this work, however, the effect of copper loading on the activity and the selectivity was investigated for the wet oxidation of phenol over  $\text{CuO}_x/\text{Al}_2\text{O}_3$  catalysts. The activity and the mineralization selectivity of the catalysts increased with copper loading up to 7 wt% and remained almost the same at a higher loading. The optimum copper loading was about 7 wt% for the wet oxidation of phenol over  $\text{CuO}_x/\text{Al}_2\text{O}_3$  catalysts in this work. The nature of copper species with different loading was characterized with TPR, XRD, and XANES. The chemical states of copper in the  $\text{CuO}_x/\text{Al}_2\text{O}_3$  catalysts were confirmed as varying with copper loading: isolated  $\text{Cu}^{2+}$  ions for 1 wt%; highly dispersed  $\text{Cu}^{2+}$  cluster for 5 wt% and 7 wt%, and bulk CuO for 10–25 wt%. The stability of the  $\text{CuO}_x/\text{Al}_2\text{O}_3$  catalysts with different copper loading was also studied with respect to carbonaceous deposits and copper leaching.

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## 1. Introduction

Wet air oxidation is the liquid phase oxidation of organics at elevated temperatures (125–320 °C) and pressures (0.5–20 MPa) using molecular oxygen as oxidant (Mishra et al., 1995; Matatov-Meytal and Sheintuch, 1998; Imamura, 1999; Pintar et al., 2004; Bhargava et al., 2006). Wet oxidation is suitable for the treatment of the wastewater which is too concentrated and/or toxic to be treated with biological approach because any organic compound could be ideally mineralized to the desired end product by wet oxidation. Various solid catalysts including the noble metal catalysts and the metal oxide catalysts have been studied for the wet oxidation of the model pollutant solution or the real wastewater.

Heterogeneous copper catalysts have been studied for wet oxidation of phenol (Sadana and Katzer, 1974a,b; Alexandre et al., 1998a,b; Alvarez et al., 2002a,b; Arena et al., 2003; Santos et al., 2005a,b). Sadana and Katzer (1974b) reported that heterogeneously catalyzed aqueous-phase phenol oxidation occurs by a free-radical mechanism which involves initiation on the catalyst surface, homogeneous propagation and either predominantly homogeneous or heterogeneous termination depending on catalyst concentration. 10 wt%  $\text{CuO}/\text{Al}_2\text{O}_3$  catalyst was tested for the wet oxidation of phenol in a triphasic tubular reactor in which the copper oxidation state of the catalyst was changed during the wet oxidation reactions (Alexandre et al., 1998b). Alvarez et al. (2002a,b) investigated a homogeneous copper catalyst and two commercial heterogeneous copper catalysts for wet oxidation of phenol; copper oxide mounted on activated carbon showed the highest activity and stability.

In our previous work (Kim and Ihm, 2005), supported transition metal oxide catalysts were tested for wet

\* Corresponding author. Tel.: +82 42 869 3915; fax: +82 42 869 5955.  
E-mail address: [skihm@kaist.ac.kr](mailto:skihm@kaist.ac.kr) (S.-K. Ihm).

oxidation of phenol. Among the catalysts,  $\text{CuO}_x/\text{Al}_2\text{O}_3$  showed the highest activity which was attributed to their superior reducibility. In this work,  $\text{CuO}_x/\text{Al}_2\text{O}_3$  catalysts with different copper loading were prepared and characterized by  $\text{N}_2$  adsorption,  $\text{N}_2\text{O}$  reactive frontal chromatography, temperature programmed reduction (TPR), powder X-ray diffraction (XRD), and X-ray absorption near edge structure (XANES) experiments. The nature of copper species, copper dispersion, Cu leaching, and carbonaceous deposits were investigated together with their activities and selectivity of phenol wet oxidation, while the optimum copper loading of  $\text{CuO}_x/\text{Al}_2\text{O}_3$  catalysts was proposed for the wet oxidation of phenol.

## 2. Experimental

### 2.1. Preparation of catalysts

$\gamma\text{-Al}_2\text{O}_3$  from STREM was used as a support for the catalysts. Copper oxide catalysts supported on  $\gamma\text{-Al}_2\text{O}_3$  with 1–25 wt% copper loading were prepared by incipient wetness impregnation method using  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  as a precursor, followed by drying at 110 °C for 12 h and calcination in air at 500 °C for 5 h. For simplicity, each catalyst will be designated according to the copper loading; for example, Cu10 denotes the catalyst loaded 10 wt% of Cu on  $\text{Al}_2\text{O}_3$ .

### 2.2. Wet air oxidation of phenol

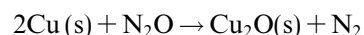
Phenol (+99% purity) was purchased from Aldrich and was used without further purification. A stirred reactor (1 l; Autoclave Co.) with suspended catalysts was used batchwise for the wet oxidation of phenol. It was equipped with a Teflon liner, magnetically driven impeller (Hastelloy), sampling line (Hastelloy), 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 the 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 by nitrogen adsorption method at liquid nitrogen temperature using Micromeritics ASAP 2000.

Cu Surface areas of the prepared catalysts were measured by reactive frontal chromatography using nitrous oxide ( $\text{N}_2\text{O}$ ) as probe molecule (Chinchen et al., 1987). The catalyst was reduced in a 5%  $\text{H}_2/\text{Ar}$  gas stream at 240 °C until no further water evolution was observed by mass spectrometry. The temperature was then lowered to 60 °C under a flow of helium until all the hydrogen had been swept from the system. The reduced material was held at 60 °C under a flow of helium which was then replaced by a 2.5%  $\text{N}_2\text{O}/\text{He}$  flow. The exposed  $\text{Cu}^0$  surface of a pre-reduced catalyst was oxidized with reactive  $\text{N}_2\text{O}$ :



where Cu (s) means the surface copper atoms. The delayed  $\text{N}_2\text{O}$  front, which is caused by the decomposition of  $\text{N}_2\text{O}$  on the exposed  $\text{Cu}^0$  surface, was monitored using mass spectrometer (QMS200M3, Pfeiffer Vacuum). Then, the  $\text{Cu}^0$  surface area was calculated with the assumption of a molar stoichiometry of  $\text{N}_2\text{O}/\text{Cu} = 0.5$  and an average value of  $1.46 \times 10^{19}$  Cu atoms  $\text{m}^{-2}$  for the surface density of copper metal.

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, POLY-SCAN 60E).

TPR of the prepared catalysts were carried out using 5%  $\text{H}_2/\text{Ar}$  gas mixture. The samples were pretreated with  $\text{O}_2$  at 400 °C for 2 h. The hydrogen consumption was recorded with TCD cell while the sample was linearly heated from 50 °C to 600 °C at 10 °C  $\text{min}^{-1}$ .

XRD patterns of the catalysts were obtained with Rigaku D/MAX-III diffractometer using monochromic Cu  $\text{K}\alpha$  ( $\lambda = 0.1506$  nm) radiation. The data were scanned from 5° to 70° ( $2\theta$ ) in steps of 0.01° and the scanning rate was 6°  $\text{min}^{-1}$ .

XANES experiments were performed for Cu K-edges at room temperature by using Beamline 3C1 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(II), Cu(I), and  $\text{Cu}^0$  standard, respectively.

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