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# High-throughput Screening of Transition Metal-doped $TiO_2$ in Photodecomposition of Phenol Under Visible Light

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**Abstract**−A catalyst library consisting of 20 catalysts with different metal and weight fraction-doped $TiO_2$ was prepared at one time for discovering the novel metal-doped $TiO_2$ photocatalyst, which is active under visible light irradiation. Combinatorial microbeam XRD and UV-vis spectrometer were used for analysis of crystal structure and photoactivity of 20 catalysts in the library, respectively. Photodecomposition of phenol was chosen as a probe reaction. The library preparation, XRD characterization and reaction test for 20 catalysts were completed within 48 hours. Among the catalysts in the library, 1.5 wt% Co/$TiO_2$ showed the best activity for phenol degradation.

Key words: Combinatorial High-throughput Screening, Photocatalyst, Phenol, Metal-doped $TiO_2$, Visible Light

## INTRODUCTION

Photocatalytic conversion of organic pollutants is a clean technology for environmental protection [Wu et al., 2002]. $TiO_2$ is the most attractive photocatalyst due to its high reactivity and nontoxicity [Ollis and Al-Ekabi, 1993; Lee et al., 2002]. But, the disadvantage of $TiO_2$ is its inactivity in the visible region. Doping $TiO_2$ with transition metal ions can extend the absorption of the band gap of $TiO_2$ to the visible region [Zang et al., 2000; Soria et al., 1991; Choi et al., 1994; Brezova et al., 1997].

Combinatorial high-throughput screening is the most promising technology in searching the novel composition of transition metal on $TiO_2$ more efficiently. In recent years, the high throughput screening for materials and catalysts has been amply demonstrated [Jandeleit et al., 1999; Baeck and McFarland, 2002], while reports on the discovery of superior novel substances are still limited.

In this paper, we introduced a high-throughput screening method for developing new photocatalysts for phenol decomposition under the visible light irradiation. The catalyst library consisting of 20 catalysts with different kinds of metal and various compositions on $TiO_2$ was prepared at one time. The analysis of crystal structure of prepared catalyst library was carried out with combinatorial microbeam XRD, which is capable of simultaneous analysis of the crystal structure of samples. The measurement of absorbance using UV-vis spectroscopy was used as an easy and fast technique for determining the photoactivity of each catalyst.

## EXPERIMENTAL

### 1. Catalyst Preparation

**Table 1. The kinds of metal precursor, solvent and the volume of added metal precursor solution for 1 wt% metal loading**

| Metal ion | Precursor | Solvent | Volume (μl) |
|---|---|---|---|
| Pt | $H_2PtCl_6$ | Isopropanol | 33 |
| Cu | $Cu(NO_3)_2 \cdot 3H_2O$ | Isopropanol | 100 |
| Fe | $Fe(NO_3)_3 \cdot 9H_2O$ | Isopropanol | 114 |
| Co | $CoCl_2 \cdot 6H_2O$ | Isopropanol | 108 |
| Ni | $Ni(NO_3)_2 \cdot 6H_2O$ | Isopropanol | 109 |

The catalyst library was synthesized in 2 ml glass vials arranged in the rack of four rows and five columns. All samples were prepared by acid-catalyzed sol-gel method. 120 μl of titanium isopropoxide was dissolved in 500 μl of isopropanol in 2 ml of glass vial. 8 μl of 8 N hydrochloric acid and calculated volume of 0.05 N metal solution was added to each vial. The weight percent of metal loading was 0.5, 1, 1.5 and 2 wt%. The kinds of metal precursor, solvent and the volume of added metal precursor solution for 1 wt% of metal loading are summarized in Table 1. Each vial was loosely covered and the rack with 20 glass vials was shaken for 24 hours by using an MS1 minishaker (IKA Works orbital shaker) with 600 rpm. After gelation, the gels were aged at room temperature and calcined at 400 °C for 3 hours as contained in a vial.

### 2. XRD

The crystal structures of the catalyst library were analyzed in the range of $2\theta$ between 20 and 80° with combinatorial micro-beam XRD (Bruker, Germany) that uses Cu $K\alpha$ radiation ($\lambda$=1.54056 Å).

### 3. High-throughput Photocatalytic Reactor and Activity Measurement

To examine the activity of the catalyst for photodegradation of water pollutants on irradiation of visible light, the degradation of phenol was chosen as a probe reaction. After calcination was ended, the vial containing a catalyst was used as a reactor without any change. 1 ml of phenol solution (10 mg $L^{-1}$) was added to each glass vial containing catalyst. The light was irradiated from eight conventional fluorescence lamps (Osram, 13W, Germany). The lamps were mount-

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‡This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

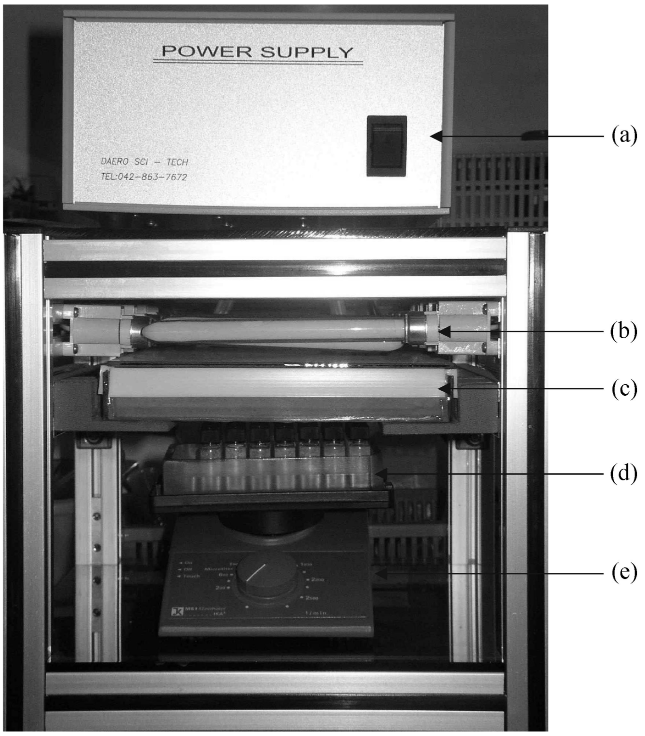

**Fig. 1. Front view of the experimental setup for visible-light irradiation of the libraries.**
(a) Power supply (b) Fluorescence lamp (c) Solution filter (d) Catalyst library (e) Shaker

ed symmetrically side by side in order to ensure homogeneous light intensity. 1 M of a potassium chromate solution was placed in a frosted-glass bath to remove UV light and to improve the homogeneity of the light-intensity distribution. The solution filter was placed between light sources and catalyst library. The sample library containing catalyst and phenol solution was aligned in the center of lamps as shown in Fig. 1. A detailed explanation of the experimental equipment was reported elsewhere [Lettmann et al., 2001]. The light was irradiated into the catalyst library after passing through the solution filter for 12 hours. The concentration of residual phenol was determined from the peak intensity of absorbance at 270 nm with UV-vis spectrometer (HP8452A Diode Array Spectrophotometer). Calibration was carried out with a range from 0.1 mg $L^{-1}$ to 10 mg $L^{-1}$ of phenol solution and good linear regression was obtained.

## RESULTS AND DISCUSSION

### 1. Analysis of Crystal Structure

Prepared 20 sample catalysts were placed on the Si wafer and the identification of each crystal structure was carried out directly with a GADDS microdiffractometer from Bruker AXS. The sample powder diffractograms were recorded with a 500 μm collimator. The library was mounted on the XYZ stage of the diffractometer and the diffractograms were obtained in the reflection mode after the step parameters were specified and the points to be measured were identified. The X-ray beam can be focused maintaining high X-ray intensity by means of bent Göbel mirrors to a diameter 50 μm, whereby individual μm-sized particles become accessible to X-ray analysis. In this reason, the analysis time required for each sample catalyst was reduced and diffractograms of 20 samples could be recorded within 3 hours.

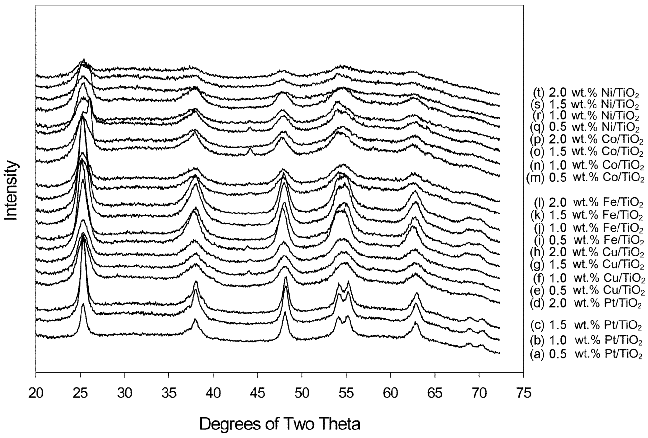

**Fig. 2. XRD profiles of 20 catalysts after calcinations at 400 °C.**

X-ray diffraction analysis of calcined samples showed that all samples revealed similar peaks regardless of the presence of metal ions and different amount of metal loading. All peaks were unique peaks representing the formation of anatase crystal structure of $TiO_2$ as shown in Fig. 2. It is well known that calcinations at 400 °C induce the formation of anatase structure of $TiO_2$. However, it is noteworthy that no specific peaks coming from metal loading were observed for any catalysts. This suggests that the imbedded metal is highly dispersed or incorporated into the support network. A similar result was also reported for sol-gel prepared metal-loaded $TiO_2$ [Pecchi et al., 2003].

### 2. Photodegradation of Phenol

Fig. 3 shows the conversion profile of phenol according to various metal loadings under visible light irradiation. Before the reaction with metal-doped $TiO_2$, the possibility of irradiation with ultraviolet light on the catalyst library was investigated with undoped $TiO_2$. The undoped $TiO_2$ was prepared by the same method as metal-doped $TiO_2$, but no metal precursor solution was added during

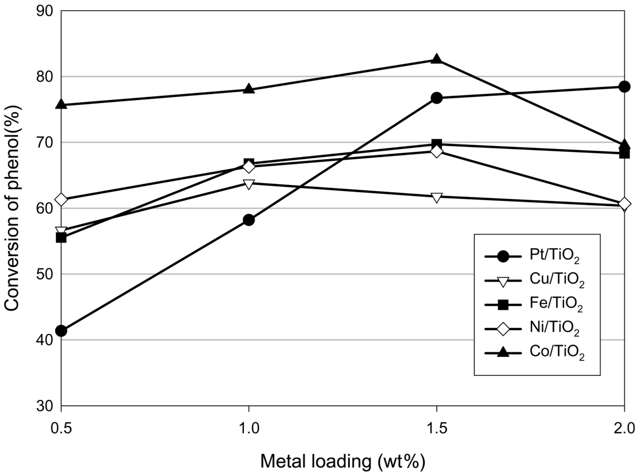

**Fig. 3. The conversion profiles of phenol for different metal-doped $TiO_2$.**

preparation. After gelation, drying and calcination, the photodegradation of phenol was carried out and no conversion was observed with undoped $TiO_2$. Complete conversion of phenol was not obtained for any metal loading for 12 hours of irradiation. For the case of Cu-, Fe- and Ni-loaded $TiO_2$, the conversion change according to the amount of metal loading was not so much. For the Pt/$TiO_2$, the activity was the lowest at 0.5 wt% of Pt loading and the conversion was 41%. With increased metal loading, the activity was gradually increased and the highest at 2 wt% loading of Pt and the conversion was 79%. For Co/$TiO_2$, the activity was comparatively higher than that of any other metal and steadily increased from 75% to 82% as the metal loading was increased to 1.5 wt%. However, the conversion was decreased to 70% at 2 wt% loading of Co. The maximum conversion among all catalysts was obtained for 1.5 wt% Co/$TiO_2$. All catalysts showed photoactivity in visible light-irradiation. It is noteworthy that Co-loaded $TiO_2$ showed a relatively high photoactivity below 1.5 wt% loading and the highest photoactivity among all metals since it was known that doping of transition metal such as Co, Fe, Ni and Cu on $TiO_2$ caused a reduction of photoactivity even though the absorption of spectrum to visible light was enhanced by adding them. Further study is required to elucidate the mechanism of photoreaction of Co/$TiO_2$ with visible light.

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