

# IRON-MODIFIED CARBON-COATED TiO<sub>2</sub> FOR ADSORPTION AND DECOMPOSITION OF PHENOL IN WATER

Beata Tryba<sup>1</sup>, Masahiro Toyoda<sup>2</sup>, Michio Inagaki<sup>1</sup>

<sup>1</sup> Aichi Institute of Technology, Yakusa, Toyota 470-0392 Japan

<sup>2</sup> Oita University, Depart. of Applied Chemistry, Dannoharu 700, Oita 870-1192, Japan

Corresponding author e-mail address: [tryba@aitech.ac.jp](mailto:tryba@aitech.ac.jp)

## Introduction

Carbon-coated TiO<sub>2</sub> catalysts were found to have high photocatalytic activity for photodecomposition of methylene blue in water, higher than TiO<sub>2</sub> without carbon coating [1]. However, these catalysts used for phenol decomposition showed lower activity than TiO<sub>2</sub> without carbon coating. Also lower adsorption capacity of phenol on carbon-coated TiO<sub>2</sub> catalysts was noted by comparison with adsorption of methylene blue [2]. Therefore, the chemical modification of carbon layer on TiO<sub>2</sub> particles is proposed in this work to increase the attraction of phenol molecules to the catalyst surface. By increasing adsorption on the catalyst surface high decomposition rate of phenol was expected.

## Experimental

PET impregnated by FeC<sub>2</sub>O<sub>4</sub> through its water solution (PET/FeC<sub>2</sub>O<sub>4</sub> = 10:1 g/g) was mixed with TiO<sub>2</sub> in mass ratio of TiO<sub>2</sub>/PET = 7/3, and heated at 400-900°C in Ar for 1 hour. Anatase-type TiO<sub>2</sub> of ST-01 (Ishihara Sangyo Co. Ltd, Japan) was used for catalyst preparation.

All samples were characterized by BET surface area, XRD, TG and FTIR. Relative concentrations of phenol solution were measured in UV-VIS spectrometer. Adsorption capacity of phenol on prepared samples was estimated in a dark, before photodecomposition. Photodecomposition of phenol was performed under UV irradiation in the "batch mode" reactor equipped with 3 black light blue fluorescent lamp of 20W power. Measured irradiation power flux of UV rays inside reactor was 1.8 mW/cm<sup>2</sup>. For measurement, 500 mL of phenol solution with initial concentration of 0.02 g/L and 0.1 g of catalyst were used. To accelerate the process of decomposition, small amount of H<sub>2</sub>O<sub>2</sub> aqueous solution of 30 mol % was added to the reaction mixture (1 ml per 1 L of phenol solution). Measurements were also performed without H<sub>2</sub>O<sub>2</sub> addition.

Rate photodecomposition of phenol was compared by the linear relation between  $\ln(c/c_0)$  and  $t$ , where  $c_0$  and  $c$  are concentrations of starting solution and that after UV irradiation in time  $t$  (h), respectively.

## Results and Discussion

Characteristics of carbon-coated TiO<sub>2</sub> catalysts together with preparation conditions are listed in Table 1.

Table 1. Characteristics of iron-modified carbon-coated TiO<sub>2</sub> catalysts

Temperature of heat treatment (°C)	Content of TiO <sub>2</sub> (mass %)	BET surface area (m <sup>2</sup> /g)	XRD (phases)	Phenol adsorption (10 <sup>-5</sup> mol/g)
400	84.5	143	A	29.2
500	89.5	150	A	2.7
600	90	143	A	4.2
700	91	142	A	3.7
800	92.5	128	A	5.3
900	93.5	139	A, R	8.2

Carbon-coated TiO<sub>2</sub> catalysts showed the structure of anatase phase, only catalyst heat-treated at 900°C containing a small amount of rutile phase. BET surface area of catalysts didn't differ so much, a little higher BET for the higher amount of carbon in the catalyst.

Surprisingly high adsorption of phenol was observed on the catalyst prepared at 400°C. For carbon-coated TiO<sub>2</sub> without iron modification prepared at 400°C, adsorption of phenol was relatively high as 19.1·10<sup>-5</sup> mol/g, but for carbon prepared from PET at the same temperature was only 1.4·10<sup>-5</sup> mol/g. This phenomenon can be explained by the chemical structure of the catalyst surface. In Fig. 1 FTIR spectra of iron-modified carbon-coated TiO<sub>2</sub> catalysts heat-treated at different temperatures are presented. On FTIR spectra it can be observed, that only catalyst heat-treated at 400°C has a special broad band at 900-1400 cm<sup>-1</sup> which may be attributed to C-O-C vibrations. This band disappeared when the samples were heated at higher temperatures. It was reported in the literature [3], that phenol molecules are adsorbed predominately on the oxygen-containing basic groups on the surface of activated carbon. C-O-C band was formed by interaction of oxidative TiO<sub>2</sub> with carbon. It was confirmed by additional investigations, that the same band is formed by heating ST-01 and PET at 400°C, and was not detected in both carbons prepared at the same temperature from PET and iron-impregnated PET.

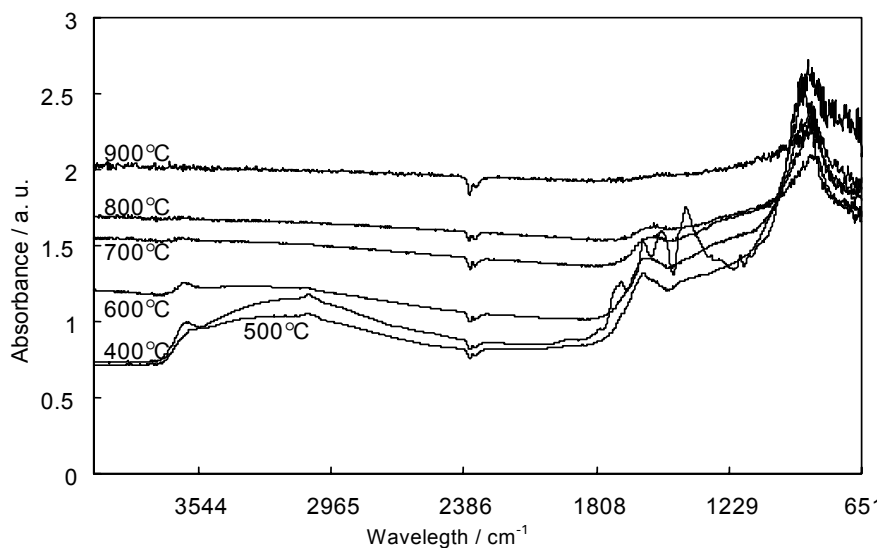


Figure 1. FTIR spectra of iron-modified carbon-coated  $\text{TiO}_2$  catalysts heated at 400-900°C

Although adsorption of phenol on iron-modified carbon-coated  $\text{TiO}_2$  prepared at 400°C increased much, decomposition of phenol under UV irradiation was still much slower than on pure ST-01, as shown in Fig. 2.

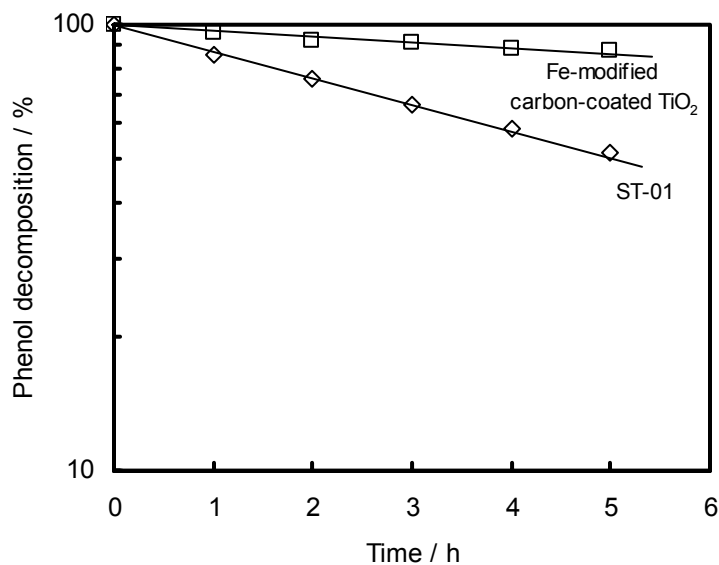


Figure 2. Decomposition of phenol under UV irradiation on ST-01 and iron modified carbon-coated  $\text{TiO}_2$  heated at 400°C

This is caused by a slow diffusion of adsorbed species to TiO<sub>2</sub> surface through the carbon layer. The iron modified carbon-coated TiO<sub>2</sub> catalysts heat treated at 500-900°C showed slow rate of phenol decomposition too. In fact, almost no phenol decomposition was noted on the catalyst heated at 500-900°C.

In order to accelerate the rate of phenol decomposition, a small amount of H<sub>2</sub>O<sub>2</sub> (1 ml per L) was added to the reaction mixture. In Fig. 3 phenol decomposition under UV irradiation supported by H<sub>2</sub>O<sub>2</sub> is presented for ST-01 and iron-modified carbon-coated TiO<sub>2</sub> catalyst heated at 400°C.

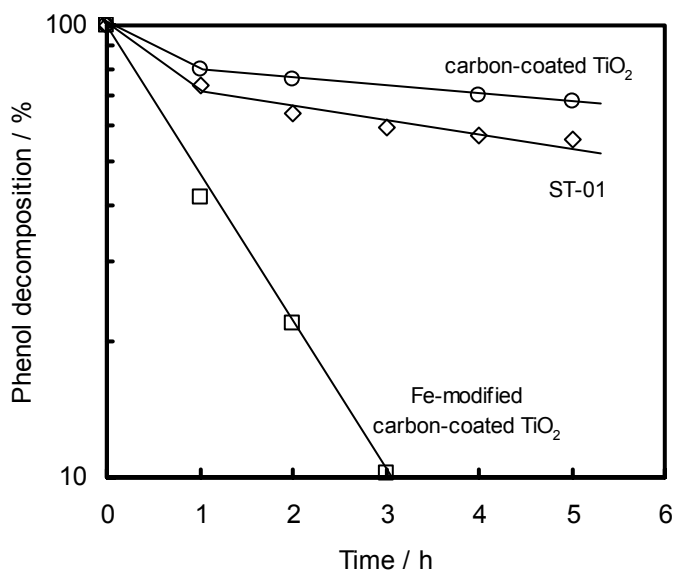
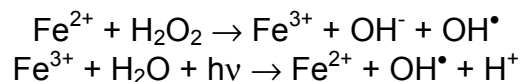


Figure 3. Phenol decomposition under UV irradiation and H<sub>2</sub>O<sub>2</sub> on ST-01, carbon-coated TiO<sub>2</sub> and iron-modified carbon-coated TiO<sub>2</sub> heated at 400°C

From Fig. 3 it is observed a high rate of phenol decomposition on iron-modified carbon-coated TiO<sub>2</sub> catalyst heated at 400°C. Anchored iron in the catalyst can catalyze the phenol adsorption, and also can give rise to hydroxyl radicals via photo-Fenton reaction by photoredox process of Fe(III) to Fe(II) and OH<sup>•</sup> [4, 5]. Fe(II) formed was supposed to be simultaneously re-oxidized to Fe(III) by oxidizing species (H<sub>2</sub>O<sub>2</sub>) in the solution:



In the case of ST-01 with the addition of H<sub>2</sub>O<sub>2</sub> didn't enhance its photocatalytic activity, probably because of recombination of reactive radicals formed from H<sub>2</sub>O<sub>2</sub> and excited TiO<sub>2</sub>.

Phenol decomposition on catalysts heat-treated at 500-900°C was much lower than on the catalyst heated at 400°C, even with the addition of H<sub>2</sub>O<sub>2</sub>.

## Conclusions

Carbon-coated TiO<sub>2</sub> catalyst prepared from PET at 400°C was found to have high adsorption capacity for phenol. A broad band at 900-1400 cm<sup>-1</sup> on FTIR spectra attributed to C-O-C vibration was found to be responsible for high phenol adsorption. Although high adsorption of phenol on iron-modified carbon-coated TiO<sub>2</sub> prepared at 400°C was achieved, the rate of phenol decomposition under UV irradiation was much lower than on TiO<sub>2</sub>. Addition of H<sub>2</sub>O<sub>2</sub> to the reaction mixture increased the rate of phenol decomposition.

Phenol can be effectively removed by using iron modified carbon-coated TiO<sub>2</sub> catalyst prepared at 400°C by combination of two processes: adsorption and decomposition under UV irradiation accelerated by photo-Fenton reaction.

## References

- [1] Tsumura T, Kojitani N, Izumi I, Iwashita N, Toyoda M, Inagaki M. Carbon coating of anatase-type TiO<sub>2</sub> and photoactivity. *J. Mat. Chem.* 2002;12:1391-1396.
- [2] Tryba B, Tsumura T, Janus M, Morawski AW, Inagaki M. Carbon-coated anatase - adsorption and decomposition of phenol in water. *Appl. Cat. B: Environm.*, in press.
- [3] Vidic R D, Tessmer CH, Uranowski L J. Impact of surface properties of activated carbons on oxidative coupling of phenolic compounds. *Carbon* 1997; 35:1349-1359.
- [4] Neamtu M, Yediler A, Siminiceanu I, Kettruo A. Oxidation of commercial reactive azo dye aqueous solutions by the photo-Fenton and Fenton-like processes. *J. Photochem. Photobiol. A: Chem.* 2003;161:87-93.
- [5] Crowther N, Larachi F. Iron-containing silicalites for phenol catalytic wet peroxidation. *Appl. Cat. B: Environm.* 2003;46:293-305.