

# PREPARATION OF CARBON-COATED TiO<sub>2</sub> PHOTOCATALYSTS FROM DIFFERENT CARBON PRECURSORS

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

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

<sup>2</sup> *Oita University, Dannoharu 700, Oita 870-1192, Japan*

*Corresponding author e-mail address: tryba@aitech.ac.jp*

## Introduction

TiO<sub>2</sub> photocatalyst is commonly used in water purification. Recently some research works were focused on modification of TiO<sub>2</sub> by carbon [1-6]. Generally two kinds of composites between TiO<sub>2</sub> and carbon were proposed, TiO<sub>2</sub>-loaded activated carbon and carbon-coated TiO<sub>2</sub>. In the case of TiO<sub>2</sub> mounted on activated carbon, it's pretty difficult to decompose all adsorbed species, so activity of this catalyst decreases with cycling [4]. Therefore the latter composite seems to be more interesting.

Modification of TiO<sub>2</sub> catalyst by carbon coating leads to increase the adsorption of organic molecules on the catalyst surface. By increasing the adsorption capacity of TiO<sub>2</sub> catalyst for the organic matters, the photodecomposition of adsorbed species under UV irradiation is expected to be accelerated. It was already proved that carbon-coated TiO<sub>2</sub> photocatalyst could enhance photoactivity of TiO<sub>2</sub> for methylene blue decomposition in water [7]. Carbon coating was performed by a simple process: mixing of TiO<sub>2</sub> with PVA carbon precursor and heating at 700-900°C under nitrogen gas.

In this paper the influence of carbon precursor on the carbon-coated TiO<sub>2</sub> catalyst is reported. As a carbon precursor, poly(ethylene terephthalate) (PET), hydroxypropyl cellulose (HPC) and poly(vinyl alcohol) (PVA) were used.

## Experimental

For catalyst preparation, anatase type TiO<sub>2</sub> (ST-01, Ishihara Sangyo Co. Ltd, Japan) and powdered PVA, PET, and HPC were used. Each polymer (P) was mechanically mixed with TiO<sub>2</sub> at different mass ratio (TiO<sub>2</sub>/P = 50/50, 60/40, 70/30, 80/20, 90/10) and heated at 900°C for 1 h in argon atmosphere.

XRD patterns of samples were recorded with scanning speed of 2°/min using CuK $\alpha$  radiation. BET surface area was measured by nitrogen adsorption at 77 K. Content of carbon in samples was measured through the combustion of carbon in air at 1000°C by using TG apparatus.

Adsorption of catalyst was performed in the dark, by mixing of catalyst with MB solution until the saturation in adsorption. Photodecomposition was conducted in the "batch

mode” reactor equipped with 3 black light blue fluorescent lamp of 20W power. This lamp emits the light at the wavelength range of 300-415 nm with maximum at 352 nm. Measured irradiation power flux of UV rays inside reactor was 1.8 mW/cm<sup>2</sup>. The reaction mixture was stirred with a magnetic stirrer. In every hour, a few ml of solution was sampled from the reaction mixture through a membrane filter in order to measure MB concentration. The concentration of MB was calculated from the height of peak at 664 nm in UV-Vis spectra, by using calibration curve. Rate constant *k* of MB photodecomposition was calculated from linear slope of the relation between  $\ln(c/c_0)$  and *kt*, where *c*<sub>0</sub> and *c* are the concentration of starting solution and that after UV irradiation in time *t* (h), respectively.

## Results and Discussion

Original ST-01 has BET surface area of 300 m<sup>2</sup>/g. Carbon-coated TiO<sub>2</sub> catalysts showed BET surface area of 50-250 m<sup>2</sup>/g, the higher BET surface area for the higher content of carbon in the catalyst. PET gave a little higher carbonization yield in comparison to HPC and PVA, and so BET surface areas of the carbon-coated catalysts using PET were higher. Content of carbon in the catalysts obtained from PVA and HPC was up to 11 mass % for using mixing ratio of TiO<sub>2</sub>/P = 50/50 but 21 mass % for the catalyst prepared from PET with the same mixing ratio used. Dependence of BET surface area on the content of carbon in the catalyst is presented in Fig. 1.

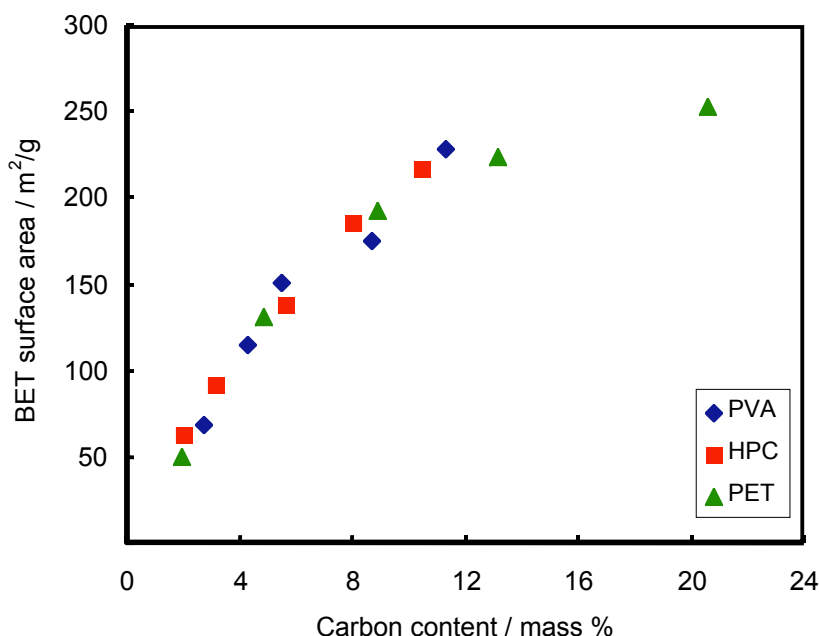


Figure 1. Dependence of BET surface area on the content of carbon in carbon-coated TiO<sub>2</sub> catalysts obtained from different carbon precursors

BET surface area of carbon-coated TiO<sub>2</sub> depends on carbon content, irrespective with carbon precursors used. This result suggests that relatively high surface area measured is mainly owing to the carbon layer on catalyst particles.

Modification of TiO<sub>2</sub> by carbon coating increased adsorption of MB on the catalyst surface. Amount of MB adsorbed on carbon-coated TiO<sub>2</sub> catalysts against BET surface area of catalysts is presented in Fig. 2.

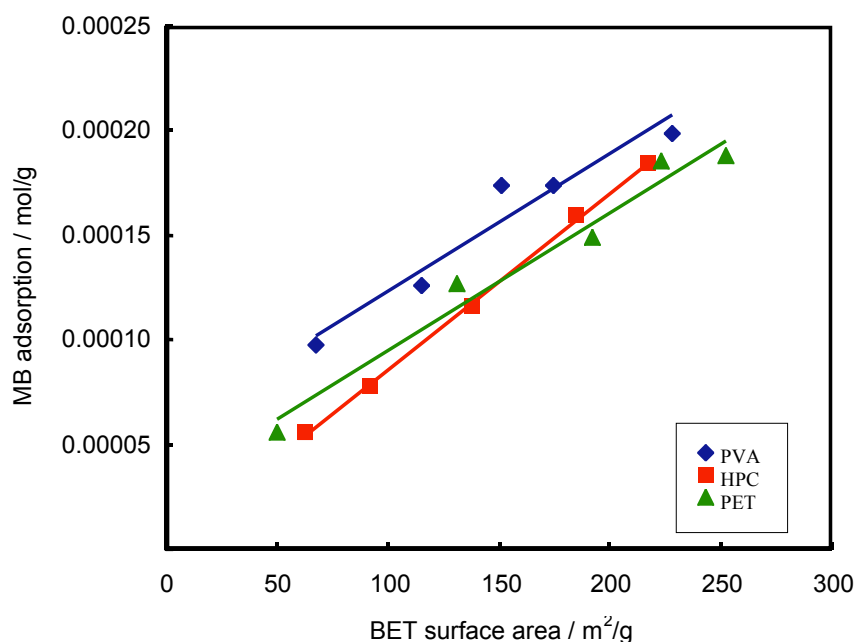


Figure 2. Dependence of MB adsorption on carbon-coated TiO<sub>2</sub> catalysts from BET surface area

Amount of MB adsorbed on the carbon-coated TiO<sub>2</sub> was in the range of 0.6 to 2·10<sup>-4</sup> mol/g, the higher for the higher BET surface area of the catalyst. The highest adsorption capacity of MB was noted on the catalysts obtained from PVA. However, there was not so much difference among the catalysts prepared by using three different precursors. Adsorption of MB was proportional to BET surface area of the catalysts and depended strongly on the content of carbon in the catalysts.

From XRD measurements it was observed that phase transformation from anatase to rutile in carbon-coated TiO<sub>2</sub> catalysts heated at 900°C was suppressed in the samples with carbon content above 5 mass %, independent on the carbon precursor used.

Calculated rate constants for MB decomposition showed the same tendency for three series of samples prepared from PET, HPC and PVA, firstly increase the rate constant with increasing the content of carbon in the catalyst and then decrease. The data are presented in Table 1.

Table 1. Calculated rate constants of MB photodecomposition for carbon-coated TiO<sub>2</sub> catalysts prepared from different carbon precursors

Mass ratio of TiO <sub>2</sub> to carbon precursor	Rate constant k (h <sup>-1</sup> )		
	Precursor		
	HPC	PET	PVA
9:1	0.15	0.06	0.16
8:2	0.23	0.30	0.19
7:3	0.41	0.34	0.27
6:4	0.25	0.42	0.37
5:5	0.32	0.30	0.24

Rate constant of MB decomposition on the starting TiO<sub>2</sub> powder without carbon coating was measured to be 0.062 h<sup>-1</sup>, much lower value in comparison with carbon-coated TiO<sub>2</sub> catalysts.

Carbon coating of TiO<sub>2</sub> increased the rate of MB decomposition in water, but there was observed the optimum of carbon content in the catalyst for which decomposition was faster. Too thick layer of carbon on TiO<sub>2</sub> particles probably slowed down the process of decomposition.

To illustrate the speed of MB decomposition In Fig. 3 the fading of MB solution with time of UV irradiation is presented on TiO<sub>2</sub> without carbon coating and carbon-coated TiO<sub>2</sub> prepared from PVA.

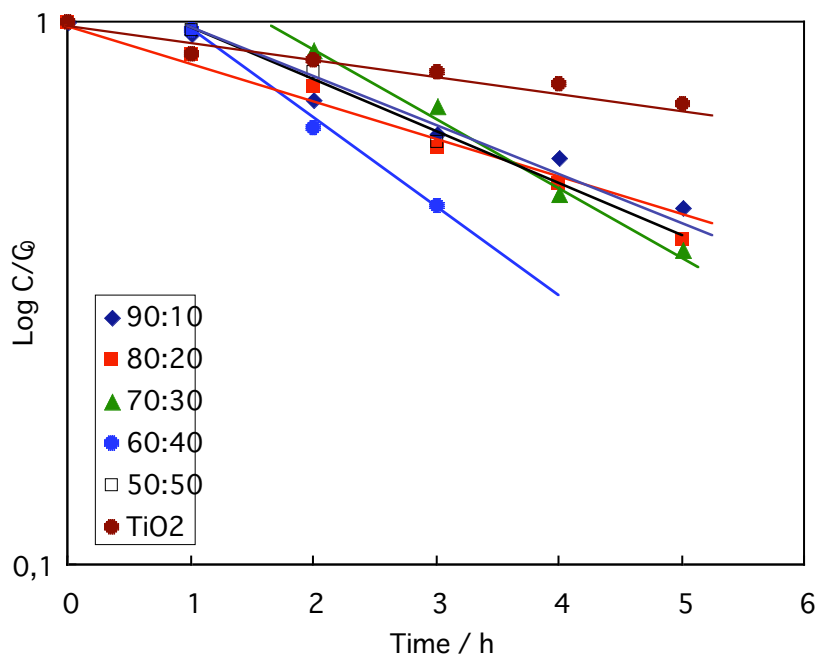


Figure 3. MB decomposition under UV irradiation on TiO<sub>2</sub> and carbon-coated TiO<sub>2</sub> catalysts prepared from PVA with different ratio of TiO<sub>2</sub> to carbon precursor

Higher rate of MB decomposition on carbon-coated TiO<sub>2</sub> catalysts than on TiO<sub>2</sub> without carbon coating can be explained by the fact that MB molecules have firstly to be adsorbed onto carbon layer and to diffuse through carbon layer before reaching on the surface of TiO<sub>2</sub> catalyst. With increasing adsorption capacity of the catalyst, therefore, decomposition rate of MB also increased.

## Conclusions

Modification of TiO<sub>2</sub> photocatalyst by carbon coating can enhance the photoactivity of TiO<sub>2</sub> for MB decomposition in water. It was proved that with increasing adsorption capacity of carbon-coated TiO<sub>2</sub> catalysts, decomposition rate of MB increased. There is not so much difference among carbon precursors used (PVA, PET, and HPC) on the properties of carbon-coated TiO<sub>2</sub> for adsorption and decomposition of MB in water. However higher adsorption of MB on carbon-coated TiO<sub>2</sub> catalysts prepared from PVA was noted, but decomposition rate of MB was mostly determined by the content of carbon in carbon-coated TiO<sub>2</sub> catalysts and phase composition of TiO<sub>2</sub>. The highest decomposition rate of MB was observed on the catalysts prepared by using mixing ratio of TiO<sub>2</sub>/P = 60/40 for PVA and PET and 70/30 for HPC. All these catalysts consisted of mostly anatase phase of TiO<sub>2</sub> and had the content of carbon in the catalyst in the range of 6-13 mass %.

## References

- [1] Tsumura T, Kojitani N, Umemura H, Toyoda M, Inagaki M. Composites between photoactive anatase-type TiO<sub>2</sub> and adsorptive carbon. *Appl. Surf. Sci.* 2002;196:429-436.
- [2] Torimoto T, Okawa Y, Takeda N, Yoneyama H. Effect of activated carbon content in TiO<sub>2</sub>-loaded activated carbon on photodegradation behaviors of dichloromethane. *J. Photochem. Photobiol. A: Chem.* 1997;103:153-157.
- [3] Nagaoka S, Hamasaki Y, Ishihara S, Nagata M. Preparation of carbon/TiO<sub>2</sub> microsphere composites from cellulose/TiO<sub>2</sub> microsphere composites and their evaluation. *J. Mol. Cat. A: Chem.* 2002;177:255-263.
- [4] Tryba B, Morawski AW, Inagaki M. Application of TiO<sub>2</sub>-mounted activated carbon to the removal of phenol from water. *Appl. Cat. B: Environm.* 2003;41:427-433.
- [5] Arana J, Dona-Rodriguez JM, Rendon ET, Cabo CG, Gonzalez-Diaz O, Herrera-Melian JA, Perez-Pena J, Colon G, Navio JA. TiO<sub>2</sub> activation by using activated carbon as a support. Part II. Photoreactivity and FTIR study. *Appl. Cat. B: Environm.* 2003;44:153-160.
- [6] Toyoda M, Nanbu Y, Kito T, Hirano M, Inagaki M. Preparation and performance of anatase-loaded porous carbons for water purification. *Dessalination* 2003;159:273
- [7] Tsumura T, Kojitani N, Izumi I, Iwashita N, Toyoda M, Inagaki M. Carbon coating of anatase-type TiO<sub>2</sub> and photoactivity. *J. Mater. Chem.* 2002;12:1391-1396.