

## Characteristics of Spherical Activated Carbon contained Titanium Oxide

*Jeong-Kwon Suh<sup>1</sup>, Joon-Jae Lee<sup>1</sup>, Ji-Sook Hong<sup>1</sup>, Young-Seak Lee<sup>2</sup> and Jung-Min Lee<sup>1</sup>*

<sup>1</sup>*Korea research Institute of Chemical Technology (KRICT), Yuseong, Deajeon, Korea, 305-600*

<sup>2</sup>*Chungnam National University, Yuseong, Deajeon, Korea, 361-810*

### Abstract

Spherical activated carbons containing TiO<sub>2</sub> (Ti-SPACs) were successfully prepared through carbonization/activation treatment. Ion exchange resin was used as a starting material of the Ti-SPAC. Ion exchanged resin and non-treated resin were activated under N<sub>2</sub>/H<sub>2</sub>O-vapor atmosphere at 900 °C for 0.5 hr, following by carbonization treatment at 700 °C under N<sub>2</sub> atmosphere. From TGA/MS analysis, main weight loss was occurred between 280 °C and 450 °C. The weight loss resulted from release of SO and CO<sub>2</sub>. The prepared Ti-SPACs and SPAC maintained spherical shape and their diameters were measured 350 ~ 400 μm from SEM image. The Ti-SPACs contained 3 wt% and 9 wt% titanium from ignition loss analysis. Rutile and anatase type TiO<sub>2</sub> were co-existed on the Ti-SPACs from XRD analysis. The Ti-SPACs containing 3 wt% and 9 wt% titanium had large BET specific surface area of 954 m<sup>2</sup>/g and 617 m<sup>2</sup>/g, respectively. From EPMA image, TiO<sub>2</sub> were uniformly distributed on the SPACs. The prepared Ti-SPACs seem to be suitable for the application as catalyst materials form adsorption capacity of activated carbon structure and photocatalytic property of TiO<sub>2</sub> on the Ti-SPAC.

Keywords : Activated carbon, Catalyst, Catalyst support, Ion exchange resin

### Intrucdution

Photocatalyst is widely used in several fields such as semiconductor, shading pigment, paint, and water purifier. At resent, application of photocatalyst was disseminated throughout environmental water purification. Undoubtedly, nano size particles bring outstanding reaction rate due to the dispersion of nano size particles that have high surface area. But photocatalyst have some problems to be applied in environmental system becauces they have nano size diameter. The limitations are a low light-utilization efficiency that is due to the absorption and scattering of the light into an aqueous suspension of illuminated powder. Indeed, the system requires post-processes such as filtration or separation process to separate the catalyst in water after the photocatalytic reaction is completed.

In general, photocatalyst is immobilized on supporters such as glass bead, silica ball, carbon, porous materials, and etc. General methods of the immobilization are CVD, impregnation, plasma coating, sol-gel method, and mechanical coating. However, these immobilization methods have some problems on their processes. First, the supporters except porous materials exhibit just as support structure and these supporters have too high specific gravity to disperse in UV/photocatalyst reactor. Second, in the case of using organic or inorganic binder to fix photocatalyst on supporter, there is possibility that surface and pore of photocatalyst are covered by the binder. Also, binder can be oxidized by hydroxyl radical and superoxide radical anion during photocatalytic reaction. What is worse, the methods are hard to immobilize photocatalyst on supporter uniformly and to control photocatalyst concentration. At recent, CVD, plasma coating and sol-gel method are widely used for photocatalyst immobilization method. Using these ways, photocatalyst can be immobilized on support uniformly. But in these methods, control of reaction condition is difficult and cost is high. Especially, when activated carbon (AC) is used as photocatalyst supporter, heat-treatments are required twice or thrice for the impregnation of photocatalyst on AC.

In the present study, the spherical activated carbons (SPACs) containing TiO<sub>2</sub> were prepared through the carbonization/activation treatment. For preparing the SPAC samples, strong acid ion exchange resin which was treated with titanium salt solution were used as starting materials. Physical characteristics of the the SPAC were measured by BET, EPMA and ESR.

## Experimental

A strong acid ion exchange resin (SK1BH, DIAION) was used as starting material of the SPAC. The strong acid ion exchange resin that consists of polystyrene and divinylbenzene (DVB) has sulfonate group as the exchangeable functional group. The resin diameter is 0.4 ~ 0.7 mm and operating pH range is from pH 1 to pH 12. This resin was treated by aqueous solution of different titanium ion concentration for 1 hr. Titanium ion concentrations were 0.15 wt% and 0.45 wt% in aqueous solution of  $TiCl_3$ . The both treated resins were activated under nitrogen/ $H_2O$ -vapor at  $900^\circ C$  for 0.5 hr.  $H_2O$ -vapor was injected at  $700^\circ C$ . In the case of the SPAC sample without titanium, the raw ion exchange resin was activated on the same condition.

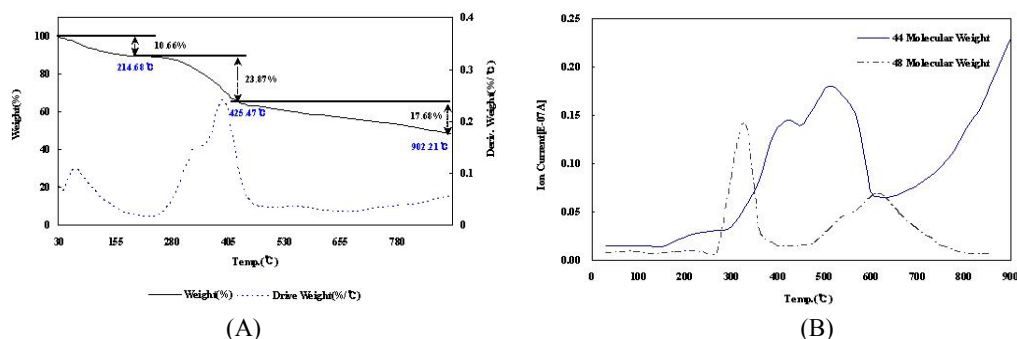
TGA (DMA, Q5000IR) and TGA/MS (VG instruments Thermostar) were used for measuring weight loss and species of gas molecule liberated during heat treatment. Morphologies and shapes of the SPAC samples were observed by SEM (JEOL, JSM-6700F). Structures of titanium compounds in the SPAC samples were identified by X-ray diffractometer (Rigaku, D/MAX- $\square$ B) with  $Cu\ \alpha$  radiation, operating at 2.0 kw. The XRD data was collected from  $20^\circ$  to  $80^\circ(2\theta)$  at scanning rate of  $0.5^\circ/min$ . For determining the spatial distribution of titanium on the SPAC samples, EPMA (JEOL, JXA-8100) and EDS (Phoenix, EDAX) were used. The specific surface area of the SPAC samples was measured by BET method (Micrometrics, ASAP 2010), after the SPAC samples were treated by degassing at  $250^\circ C$  for 6 hrs. The photochemical activity was measured by ESR (JEOL, JES-FA100). ESR measurements were performed under UV irradiation, 20 A current and 500 kHz amplitude. After the SPAC samples were fired at  $900^\circ C$  under air atmosphere for 3 hrs, residues of the SPAC samples were measured by a chemical balance for measuring titanium content in the SPAC.

## Results and Discussion

### Phenomena during SPAC preparation

In this study, strong acid ion exchange resin that was starting material of Ti-SPAC was treated by 0.15 wt% and 0.45 wt% of  $TiCl_3$  solution for 1hr. After ion exchange treatment, the treated resins had 1.5 wt% and 4.5 wt% titanium by measuring the weight of residues.

As showing in Figure 1, TGA and TGA/MS were used for measuring weight loss and species of gas molecule liberated during heat treatment. At first, 10.66 wt% of remained water in resin vaporized between  $30^\circ C$  and  $150^\circ C$ . Main weight loss was appeared from  $280^\circ C$  to  $450^\circ C$  that value was 23.87 wt% and then weight loss of 17.68 wt% was occurred until  $900^\circ C$ . Therefore, total weight loss was measured to be 52.21 wt% from room temperature to  $900^\circ C$ . During heat treatment, the weight loss was due to two different molecules that having molecular weight of 44 and 48 by TGA/MS result. The gases were inferred  $CO_2$  and  $SO_2$  because the resin has C, O, S and H component. The  $SO_2$  gas was originated from sulfonate group from  $280^\circ C$  to  $380^\circ C$  and from  $530^\circ C$  to  $720^\circ C$ . In case of  $CO_2$  gas, the  $CO_2$  gas was appeared above  $320^\circ C$ . As the result, when strong acid ion-exchange resin was used for starting material of the SPAC, sulfonate group and carbon component in resin mainly caused weight loss during heat-treatment.



**Figure 1.** TGA and derived weight curves of the Ti-SPAC and ion current changes as gas molecular weight during heat treatment : (A) TGA and derived weight curves, (B) TGA/MS.

### Characteristics of the SPAC

Figure 2. shows SEM-image of the Ti-SPAC samples. All samples were maintained their spherical shape after activation treatment. The shape of the SPAC with or without titanium had spherical with a diameter from 350  $\mu\text{m}$  to 400  $\mu\text{m}$ .

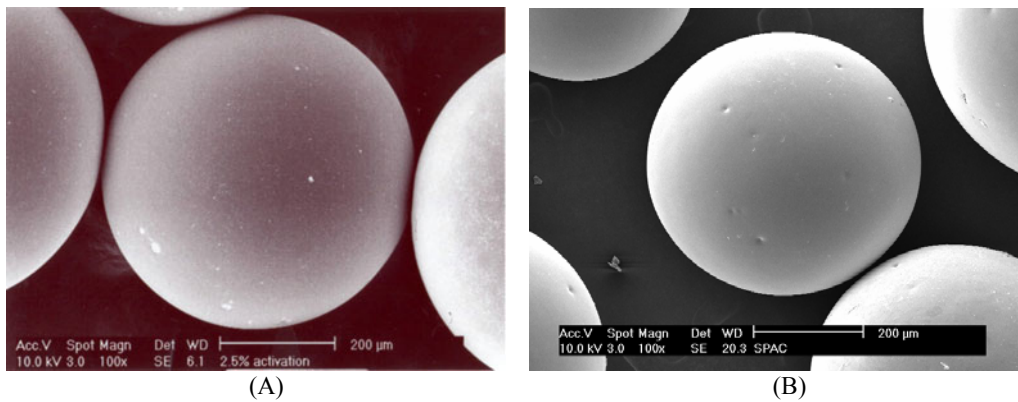
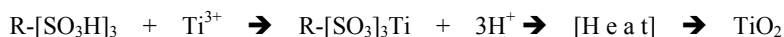


Figure 2. SEM image : (A) the Ti-SPAC, (B) the SPAC.

Structures of titanium compounds in SPAC sample were identified by X-ray diffractometer. In the Ti-SPAC, the diffraction peaks corresponding to  $\text{TiO}_2$  appeared as showing in Figure 3. Anatase and rutile type  $\text{TiO}_2$  co-exist in the SPAC. Following by below equation, titanium in resin was formed into anatase type  $\text{TiO}_2$  through heat-treatment that temperature range was from room temperature to  $800^\circ\text{C}$  and then some anatase type  $\text{TiO}_2$  was transformed into rutile type  $\text{TiO}_2$  through activation treatment. That reason was anatase type  $\text{TiO}_2$  is transformed into rutile type  $\text{TiO}_2$  over  $800^\circ\text{C}$ . Ti-SPAC have suitable photochemical activity for using photocatalyst, because composite  $\text{TiO}_2$  of anatase and rutile usually have better photocatalytic activity than photocatalytic activity of single  $\text{TiO}_2$  type.



After the Ti-SPAC samples were fired at  $900^\circ\text{C}$  under air atmosphere for 3hrs, residues of Ti-SPAC samples were measured by a chemical balance for measuring titanium content in Ti-SPAC. The residues of Ti-SPAC samples were  $\text{TiO}_2$ . The resins which were treated by 0.15 wt% and 0.45 wt% of  $\text{TiCl}_3$  solution had 5 wt% and 15 wt% of  $\text{TiO}_2$ , respectively.

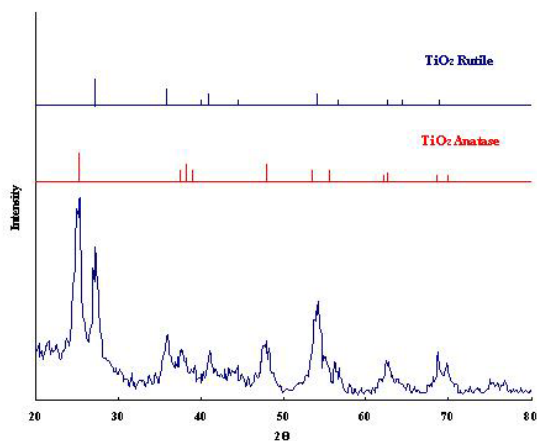
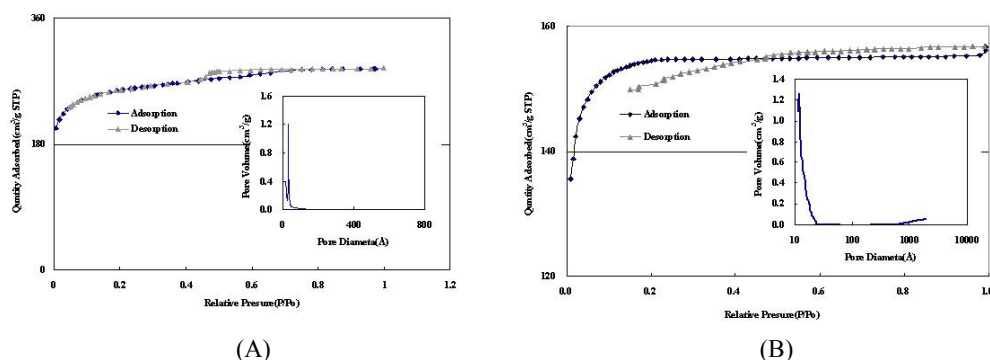
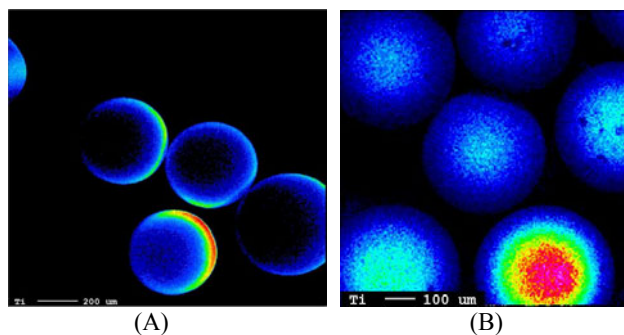


Figure 3. XRD pattern of the Ti-SPAC.

The adsorption-desorption isotherm of the Ti-SPAC samples exhibits a typical reversible type IV curve without hysteresis loops as showing in Figure 4. Figure 4. (A) is adsorption-desorption isotherm of the Ti-SPAC contained 3 wt% titanium and Figure 4. (B) is that of the Ti-SPAC contained 9 wt% titanium. SPAC sample without titanium of adsorption-desorption isotherm was similar to Ti-SPAC contained 3 wt% titanium. Furthermore, an interesting feature of the isotherms is the well-defined capillary condensation step at very low relative pressure ( $P/P_0 = 0 \sim 0.15$ ). The inset in Figure 4. (A) and (B) show the pore size distribution plots calculated using the BJH (Barrett-Joyner-Halenda) equation from the desorption branch of the isotherm. The pore size distribution measurements showed that the Ti-SPAC had pronounced microporosity of a narrow pore size distribution with main pore diameter of  $10 \sim 15 \text{ \AA}$ . The BET surface area of the Ti-SPAC containing 3 wt% titanium and the Ti-SPAC containing 9 wt% titanium were about  $954 \text{ m}^2/\text{g}$  and  $617 \text{ m}^2/\text{g}$ , respectively and the SPAC without titanium had almost the same BET surface area with the Ti-SPAC containing 3 wt% titanium. Adsorption mechanism of activated carbon that was used as supporter of  $\text{TiO}_2$  was due to promote  $\text{TiO}_2$  photodegradation.

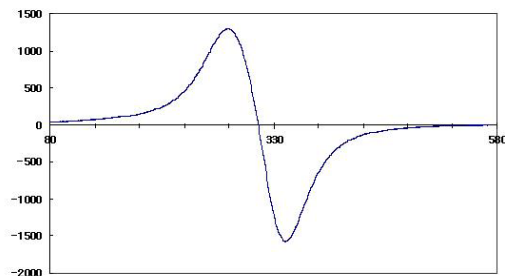


**Figure 4.** Nitrogen adsorption-desorption isotherms and the corresponding pore-size distribution (inset) of the Ti-SPAC : (A) 3 wt%, (B) 9 wt%.



**Figure 5.** EPMA image of the Ti-SPAC : (A) 3 wt% (B) 9 wt%.

EPMA is a commonly used mean to determine the spatial distribution of major elements. So titanium distribution on the SPAC was determined by EPMA. Figure. 5 is EPMA results of the Ti-SPAC contained 3 wt% titanium (A) and the Ti-SPAC contained 3 wt% titanium (B). Titanium was uniformly distributed on a unit of the Ti-SPAC sample as showing in the Figure. 6.



**Figure 6.** ESR spectrum for Ti-SPAC under UV irradiation.

ESR studies have been carried out to verify the existence of paramagnetic species such as  $\bullet\text{OH}$  and  $\text{HO}_2\bullet$  on UV irradiation of photocatalyst. Figure. 6 shows ESR spectra of the Ti-SPAC sample. Commonly, the intensity of ESR absorption is proportional to the concentration of the free radical or paramagnetic materials present. Therefore, it could be possible to produce paramagnetic species of Ti-SPAC sample under UV irradiation.

### Conclusion

We could get the spherical activated carbon (SPAC) containing  $\text{TiO}_2$ , which were uniformly dispersed on the SPAC. The Ti-SPAC samples were prepared through the carbonization/activation of treating strong acid ion exchange resin with  $\text{TiCl}_3$  solution. These Ti-SPAC samples had both characteristics of activated carbon (large BET specific surface area) and photocatalyst (producing paramagnetic species on UV irradiation). Therefore, the Ti-SPAC presented possibility of photocatalyst for water purification. Also, hazardous pollutants were easily removed or transformed to harmless substances, because the use of these samples could be possibly facilitate the adsorption of pollutants by supporter, AC, and photodegradation of pollutants by the photocatalyst.

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