

## Preparation of Ultra Fine Metal Compounds Highly Dispersed in the Porous Carbon Matrix from Ion Exchanged Resin

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We proposed a MIER-CTR (Metal Ion Exchanged Resin Carbothermal Reduction) method in which nano-scale ultra fine metallic compounds were highly dispersed in carbon matrix with large surface area by simultaneous thermal decomposition of organic resin and aggregation of metal ions by carbothermal reduction of the metal ion exchanged resin. When the chelate resin containing  $Ti^{4+}$  (CR11- $Ti^{4+}$ ) was carbonized at 500-800°C with pre-heat treatment at 350°C in air stream, the high dispersion of ultra fine particles of  $TiO_2$  (anatase) of 3-5nm size in the carbon matrix was confirmed by TEM observation. When bi-metallic CR11-( $Ti^{4+}$  and  $Pd^{2+}$ ) was carbonized,  $TiO_2$  (anatase)-Pd (metal) was formed in the porous carbon matrix. The size of  $TiO_2$  crystallites was increased from 3-5nm to 10-15nm compared to the  $TiO_2$  size of carbonized materials of mono-metallic CR11- $Ti^{4+}$ . The anatase-rutile transformation of  $TiO_2$  starts at about 800°C. In this method, when CR11- $Ti^{3+}$  was carbonized at 500°C with pre-heat treatment at 350°C in air stream,  $TiO_2$  (rutile) was formed in the carbon matrix. However,  $TiO_2$  (only anatase) was prepared in the porous carbon from CR11- $Ti^{4+}$  by carbonization at 800°C.

Key words : Ion exchange resin, Ultra fine metal compound, Porous carbon, Carbonization, Anatase, Rutile

### 1. Introduction

Activated carbons are very important as versatile adsorbents and catalyst support etc. Recently, the production of porous carbon materials with metal compounds by carbonization processes using metal ion exchanged resins has been reported [1-3]. We have reported a carbothermal reduction process for metal ion exchanged resins (MIER-CTR method) in which nano-scale ultra fine metallic compounds, W and Mo compounds, were highly dispersed in the porous carbon which had controlled pore structure [4]. The metal-oxide, -carbide, -nitride and -sulfide could be produced by the selection of ion exchange resin, metal ion and heat-treatment conditions. From the viewpoints of the preparation of highly active catalysts or adsorbents, the controls of both size of metal compounds and pore structure of porous carbon are

important. Actually, the influence of particle size of  $TiO_2$  on photocatalytic degradation of organic compounds has been studied [5]. It has been reported, that photocatalytic activity of  $TiO_2$  increased as the particle size became smaller than 30nm. In this study, we examined the preparation of nano-scale ultra fine  $TiO_2$ -carbon composite materials and the control of crystalline phase of  $TiO_2$  in the carbon matrix.

### 2. Experimental

#### Preparation of the $TiO_2$ -porous carbon composite

A commercial chelate resin having a di-imino acetic acid ( $-C-N-(COONa)_2$ , CR11: Mitsubishi Chemical Co. Ltd.) was used as a raw material. The resin was exchanged with  $Na^+$  (CR11- $Na^+$ ) or  $H^+$  (CR11- $H^+$ ) by a conventional ion exchange procedure. The CR11- $Na^+$  was exchanged with  $Ti^{3+}$  (CR11- $Ti^{3+}$ ) in

an aqueous TiCl<sub>4</sub> solution (0.2mol/l) in a glass column. As TiCl<sub>4</sub> is unstable in air, 0.05mol of TiCl<sub>4</sub> was added directly to the CR11-H<sup>+</sup>(50g) immersed in deionized water at 0°C for the exchange of Ti<sup>4+</sup> (CR11-Ti<sup>4+</sup>). This resin was then impregnated at room temperature for 25hr. The bi-metallic CR11-Ti<sup>4+</sup>-Pd<sup>2+</sup> was prepared by impregnating CR11-Ti<sup>4+</sup>(10g) with a 0.5mmol PdCl<sub>2</sub> aqueous solution for 25hr. The ion-exchanged resins were washed with deionized water, and dried at room temperature for one day. Next, these resins were pre-heat-treated (pre-HT) at 300-350°C for 1.5hr in an air stream (300ml/min). Then, N<sub>2</sub> stream was fed into the reactor (300ml/min), and the temperature was raised to the carbonization temperature (T<sub>c</sub>) at a constant rate of 5°C/min, and held at T<sub>c</sub> (500-900°C) for 3hr.

The crystalline compounds in the carbonized materials were identified by powder X-ray diffraction (XRD, SHIMAZU XD-3A). Especially, the crystalline phase of TiO<sub>2</sub> was confirmed by raman spectrum (JOBIN YVON T64000), too. The surface of the samples was observed by transmission electron microscope (TEM). The pore structure of the carbonized materials was characterized by the N<sub>2</sub> adsorption-desorption method at -196°C (BEL Japan ; BELSORP 28SP).

### 3. Results and discussion

#### 3.1 Crystalline compound of TiO<sub>2</sub>-carbon composites

Table I shows the preparation conditions and characterization of the carbonized materials. When CR11-Ti<sup>3+</sup> was carbonized at 500°C, crystalline

compounds were not confirmed by XRD (No.1 in Table I ). However, with pre-HT at 300°C in air stream, TiO<sub>2</sub> (rutile) was produced in the carbon matrix by carbonization at 500°C (No.2). TiO<sub>2</sub> (rutile) was confirmed by raman spectrum, too (Fig.1(a)(b)). When CR11-Ti<sup>4+</sup> was carbonized at 800°C(No.5) and with pre-HT at 300°C(No.6), crystalline compounds were not produced. However, only anatase of TiO<sub>2</sub> was confirmed by both XRD (No.7-9) and raman spectrum (Fig.1 (c) (d)) when CR11-Ti<sup>4+</sup> was carbonized at 500-800°C with pre-HT at 350°C. Ti contents in the carbon matrix of these carbonized materials were 0.06-0.46 [g/g-cat.]. The composites from CR11-Ti<sup>4+</sup> gave higher Ti content than ones from CR11-Ti<sup>3+</sup>.

Thermodynamically, the anatase-rutile transformation diagram (Fig.2)[6] shows TiO<sub>2</sub> (anatase) is unstable above 800°C. In practice, it has been reported, that the transformation of TiO<sub>2</sub> crystalline starts at 600-700°C from anatase to rutile [7][8]. However, TiO<sub>2</sub> (anatase) was obtained at even 800°C. Despite carbonization at low temperature (500 °C ), TiO<sub>2</sub> (rutile) was also produced in the carbon matrix by the MIER-CTR method.

Furthermore, during the MIER-CTR treatment, titanium nitride (TiN) was produced by the carbonization at 800°C of CR11-Ti<sup>3+</sup> (No.3) and by the thermal treatment at 900°C with pre-HT at 350°C of CR11-Ti<sup>4+</sup> (No.9). TiN was also produced by the carbonization of CR11-Ti<sup>3+</sup> in an argon atmosphere at 800 °C (No.4). Accordingly, nitrogen atoms of TiN crystalline were supplied by di-imino acetic acid

Table I Preparation conditions and characterization of the TiO<sub>2</sub>-carbon composite

No.	Raw material <sup>1)</sup>	pre-heat <sup>2)</sup> treatment Temp [°C]	carbonization <sup>3)</sup> Temp [°C]	Yield [g/g-dry]	Crystalline compounds	Metal compounds contents [g/g-cat]	S <sub>BET</sub> [m <sup>2</sup> /g-cat]	V <sub>p</sub> [ml/g-cat]
1	CR11-Ti <sup>3+</sup>	non	500 in N <sub>2</sub>	0.32	no peak	0.06	290	0.28
2	CR11-Ti <sup>3+</sup>	300	500 in N <sub>2</sub>	0.50	TiO <sub>2</sub> :rutile	0.10	470	0.60
3	CR11-Ti <sup>3+</sup>	non	800 in N <sub>2</sub>	0.31	TiN	0.13	350	
4	CR11-Ti <sup>3+</sup>	non	800 in Argon	0.30	TiN	0.11	230	
5	CR11-Ti <sup>4+</sup>	non	800 in N <sub>2</sub>	0.29	no peak	0.18	210	0.23
6	CR11-Ti <sup>4+</sup>	300	500 in N <sub>2</sub>	0.48	no peak	0.11	330	0.55
7	CR11-Ti <sup>4+</sup>	350	500 in N <sub>2</sub>	0.24	TiO <sub>2</sub> :Anatase	0.22	360	0.59
8	CR11-Ti <sup>4+</sup>	350	800 in N <sub>2</sub>	0.21	TiO <sub>2</sub> :Anatase	0.25	360	0.51
9	CR11-Ti <sup>4+</sup>	350	900 in N <sub>2</sub>	0.24	TiN	0.22	410	0.59
					TiO <sub>2</sub> :Anatase	0.46		
10	CR11-Ti <sup>4+</sup> -Pd <sup>2+</sup>	350	500 in N <sub>2</sub>	0.15	Pd	0.04	330	0.57

1) Raw materials Ti<sup>4+</sup>:TiCl<sub>4</sub>, Ti<sup>3+</sup>:T 2) r.t →(5°C/min)→Pre-heat-treatment temp.(1.5hr) in Air (300ml/min)

3) Pre-heat-treatment Temp.(0.5hr)→(5°C/min)→carbonization Temp.(3hr) in N<sub>2</sub> (300ml/min)

groups of the chelate resin (CR11). The bi-metallic  $\text{TiO}_2$  and Pd porous carbon composite was also prepared by this method (No.10).

Effect of the pre-HT process was examined. Fig.3 shows the FT-IR pattern of carbonized materials taken immediately after pre-HT at  $350^\circ\text{C}$ . In the IR spectrum, the vibration spectrum of C-Hn ( $n=1-3$ ) ( $3000\text{cm}^{-1}$ ) disappeared, and the spectrum of C=O ( $1700\text{cm}^{-1}$ ) remained by heating at  $350^\circ\text{C}$  in air stream. The raman spectrum and XRD analysis suggest that  $\text{Ti}^{4+}$  in CR11 were converted to  $\text{TiO}_2$  by pre-HT at  $350^\circ\text{C}$ . These results suggest that both raw carbon and Ti ion were oxidized by oxygen atoms that were included in the carbon matrix during pre-HT( $350^\circ\text{C}$ ) before the carbonization process ( $600-800^\circ\text{C}$ ).

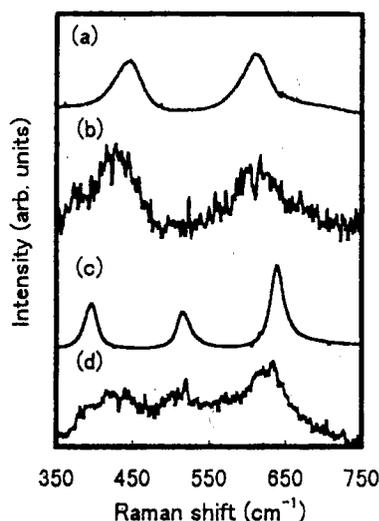


Fig.1 Raman spectra of carbonized materials (a) Rutile(Ref.), (b)CR11-Ti<sup>3+</sup>(No.2) (c)Anatase(Ref.), (d)CR11-Ti<sup>4+</sup>(No.7)

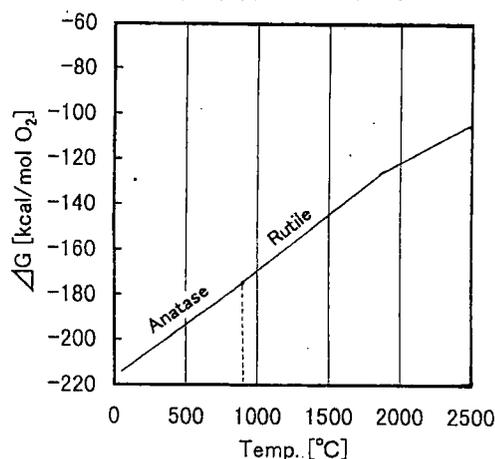


Fig. 2 Relationship between temperature and the standard free energy of formation of  $\text{TiO}_2$ <sup>(6)</sup>

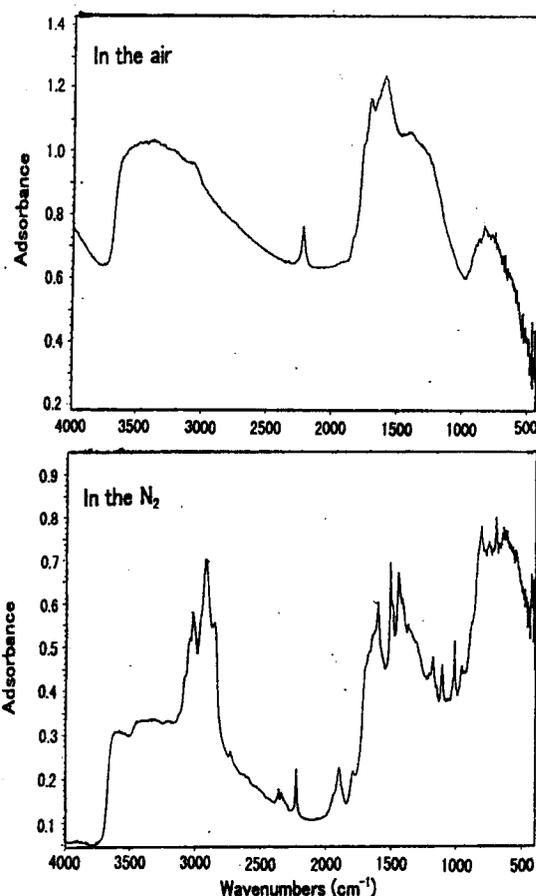


Fig. 3 FT-IR spectra after pre-HT at  $350^\circ\text{C}$  of CR11-Ti<sup>4+</sup>

### 3.2 Crystallite size of crystalline phases

The distribution of  $\text{TiO}_2$  and Pd in the carbonized material of CR11-Ti<sup>4+</sup> and CR11-Ti<sup>4+</sup>-Pd<sup>2+</sup> (No.7,10 in Table I ) was observed by transmission electron microscope (TEM). The images are shown in Fig. 4. The diameter of  $\text{TiO}_2$  particles was 3-5nm in the carbon matrix prepared by carbonization of CR11-Ti<sup>4+</sup>.(Fig.4(a)). Fig.4(b) shows the whole image and Fig.4(c) shows the local TEM images of carbonized materials of CR11-Ti<sup>4+</sup>-Pd<sup>2+</sup>. The CR11-Ti<sup>4+</sup> obtaining Pd was dispersed Pd particles of 10-15nm size (b).  $\text{TiO}_2$  particles were concentrated around Pd particles were dispersed in the carbon matrix (c). Size of  $\text{TiO}_2$  crystalline was increased from 3-5nm to 10-15nm compared to the carbonized material of CR11-Ti<sup>4+</sup> (only). These results indicate that Pd<sup>2+</sup> accelerated the growth of  $\text{TiO}_2$  crystallite.

### 3.3 Pore structure of $\text{TiO}_2$ -carbon composites

The surface area and pore volume of the sample

No.2, in Table I the CR11-Ti<sup>3+</sup> carbonized materials at 500 °C ( $S_{\text{BET}}=470\text{m}^2/\text{g}$ ,  $V_p=0.6\text{ml/g}$ ) with pre-HT, were larger than sample No.1 without pre-HT ( $S_{\text{BET}}=290\text{m}^2/\text{g}$ ,  $V_p=0.28\text{ml/g}$ ). The carbonized CR11-Ti<sup>4+</sup> showed the same tendency as the CR11-Ti<sup>3+</sup>. These results suggest that the pre-HT condition before the MIER-CTR processing control the pore structure of the carbonaceous material.

#### 4. Conclusion

We proposed a novel preparation method (MIER-CTR) for ultra fine TiO<sub>2</sub> particle highly dispersed in the

porous carbon matrix from the chelate resin. The feature of this method are : (1) The diameter of TiO<sub>2</sub> (anatase) particles was very fine ; 3-5nm in the carbon matrix prepared by carbonization of CR11-Ti<sup>4+</sup>. (2) When CR11-(Ti<sup>4+</sup> and Pd<sup>2+</sup>) was carbonized, the size of TiO<sub>2</sub> crystals increased from 3-5nm to 10-15nm. (3) Titanium ions in the resin converted TiO<sub>2</sub> and polymer carbon chain were activated by oxygen atoms supplied in the carbon matrix during the pre-heat treatment (pre-HT) in the air. (4) The activated porous carbon matrix had large surface area and pore volume in the range of micropore.

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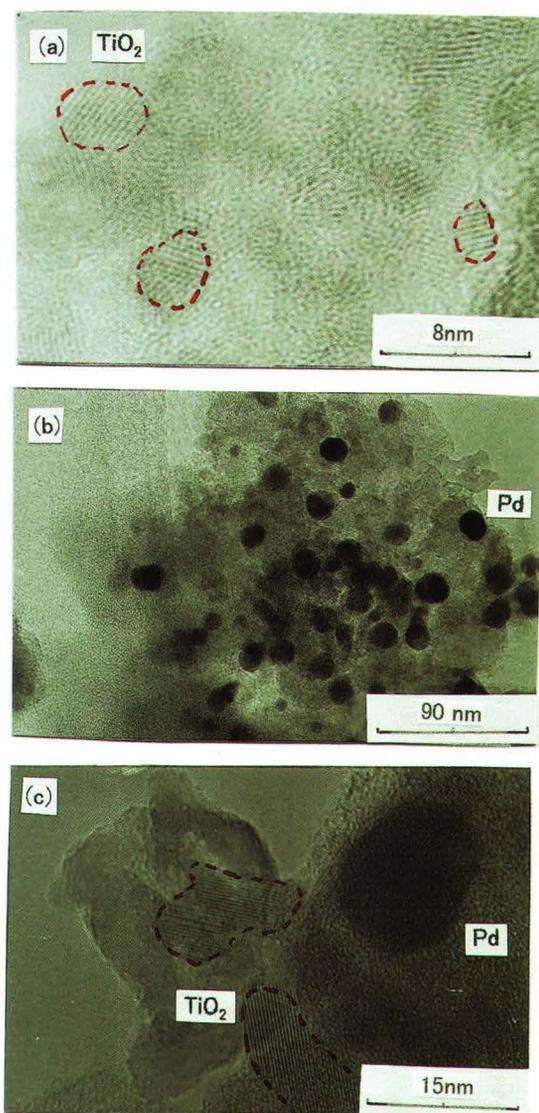


Fig. 4 TEM images of carbonized materials of (a) CR11-Ti<sup>4+</sup>, (b) and (c) CR11-Ti<sup>4+</sup>-Pd<sup>2+</sup>