

Pore structure of carbon coated on ceramic particles

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Introduction

Carbon coating of ceramic particles through a simple procedure was developed; a powder mixture of ceramic particles with carbon precursor, such as PVC and PVA, was heated at a temperature between 700 and 1100 °C in inert atmosphere, [1]. Carbon coating of TiO₂ particles was successfully carried out through sol-gel method using PVA aqueous solution [2]. This procedure has been applied on various ceramics, such as different aluminum oxides, magnesium oxide, titanium oxide, various iron oxides, nickel oxide, natural graphite, etc., and also on ceramic tiles and aluminum plate of which surface was electrochemically oxidized.

Carbon coating on photocatalytic anatase-type TiO₂ was found to give various advantages [3,4]. Carbon layer formed on TiO₂ was supposed to be very porous and ultraviolet rays was experimentally proved to reach the substrate TiO₂ [5]. On these carbon-coated TiO₂, the species, which had to be decomposed such as methyleneblue and phenol in our series of works, had to be adsorbed on the carbon layer and then to diffuse onto the surface of catalyst particles TiO₂. Therefore, adsorptivity of carbon layers is one of determining factors for the performance of carbon-coated TiO₂. Since these carbon-coated catalysts were found to have relatively high adsorptivity for methyleneblue in aqueous solution, carbon formed on TiO₂ particles was supposed to be porous. However, we could measure only overall value of BET surface area on the carbon-coated particles, not that on carbon layer coated.

In the present work, therefore, pore structure of carbon layer, which was coated on MgO particles was studied in detail after dissolving out the substrate MgO. Carbon coating on TiO₂ particles was then performed from different carbon precursors.

Experimental

MgO (reagent grade), of which particle size was about ?? mm and BET surface area was about 7 m²/g, was selected because it can be easily dissolved out by sulfuric acid to isolate carbon formed on its surface. TiO₂ was a commercially available powder with anatase- type structure (ST-01), of which photocatalytic activity was studied in our previous works [3,4]. The size of primary particles of TiO₂ was about 7 nm by means of X-ray diffraction (XRD) and that of aggregated secondary particles was about 60 nm by SEM. Carbon precursors used in the present work were poly(vinyl alcohol) PVA, poly(ethylene terephthalate) PET and hydroxy-propyl cellulose HPC.

Carbon coating of ceramic powders was carried out as follows; a powder mixture of ceramic powder to carbon precursor polymer in different ratios (from the ratio of 30/70 to 90/10 in mass) was heated in a flow of argon at a temperature of 900 °C for 1 h.

Adsorption/desorption isotherms of nitrogen gas were measured at 77 K on the

carbon-coated powders and analyzed by BET method. The amount of carbon coated was determined from weight loss of the sample heated at 1000 °C for 1 h in air in TG apparatus. For carbon-coated MgO powders, substrate MgO was dissolved out by using 3 mol/L sulfuric acid at room temperature and carbon formed on its surface was recovered, on which BET, a_s and DFT analyses were performed.

Results and discussion

Carbon coated on MgO

After heat treatment with PVA at 900 °C, white MgO powders changed to black, no white particles were found even under optical microscope.

In Table 1, the values of carbon content and BET surface area determined by two methods are tabulated. Carbon contents determined by burning-off at 1000 °C coincide with those determined as recovery ratio after dissolving MgO. Apparent BET surface area measured on carbon-coated MgO decreases with increasing mixing ratio of MgO/PVA. From these apparent values and carbon content determined by burning-off, BET surface area of carbon layers was calculated under the assumption that the substrate MgO does not have any surface area and listed in Table 1. These calculated surface area values show pretty good agreement with BET surface area measured directly on the isolated carbon by dissolving MgO. BET surface area of carbon layers coated on MgO surface is very high, 1000-1400 m²/g, although any activation process is not included during their preparation.

The analysis using a_s plot was applied on desorption isotherm of each carbon isolated from MgO and also DFT analysis was performed to compare the pore size distribution in the micropore region. The pore parameters determined from a_s plots are summarized in Table 2 and pore size distributions determined by DFT method were shown in Fig. 1.

Table 1 Content and BET surface area of carbon coated on MgO particles

Mixing ratio (mass)	Carbon content (mass%)		BET surface area (m ² /g)		
	Burn-ing ¹	Dissolution ²	Apparent ³	Calculated ⁴	Measured ⁵
MgO/PVA 30/ 70	18.7	17.3	241	1290	984
	17.9	20.6	143	800	925
50/50	6.9	7.1	85	1200	1200
	7.0	6.1	99	1400	1450
70/30	2.6	2.8	34	1120	1210
	2.7	3.7	38	1130	1040

¹ Carbon content determined by burning off at 1000°C in air.

² Carbon content determined by dissolution of MgO in 3 mol/L H₂SO₄ solution.

³ BET surface area determined on carbon-coated MgO particles.

⁴ BET surface area calculated from carbon content determined by burning-off under the assumption that MgO particles has no surface area.

⁵ BET surface area measured on carbon isolated through dissolution of MgO by H₂SO₄.

Carbons prepared from the 70/30 and 50/50 mixtures show relatively large micropore volume, though somewhat different distribution in micropore size, in comparison with that from the 30/70 mixture. Relatively low surface areas and small micropore volume on carbon derived from 30/70 mixture seems to be due to large

carbon content. Other two carbon samples give very high surface areas and micropore volume. These experimental results suggest that the interface regions between carbon formed from PVA and MgO particle has a definite role to make carbon layer porous. In the present system for the carbonization, any oxidation process, *i.e.*, activation, was difficult to be included, because no change in MgO was detected either by X-ray diffraction or X-ray photoelectron spectroscopy.

Table 2 Parameters of pore structure determined from the analysis using a_s plot on isolated carbons from carbon-coated MgO.

Mixing ratio MgO/PVA (in mass)	Total surface area (m^2/g)	Microporous surface area (m^2/g)	Micropore volume (mL/g)
30/70	1080	828	0.24
50/50	1600	1350	0.49
70/30	1270	1110	0.42

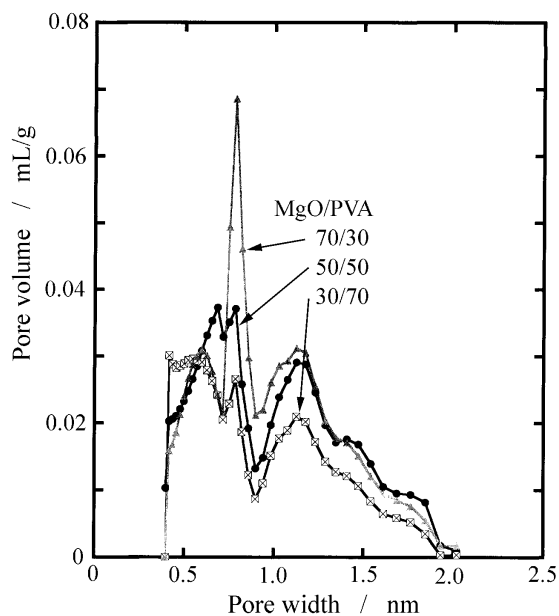


Fig. 1 Pore size distribution in the micropore range measured by DFT method.

Carbon coated on TiO_2

On carbon-coated TiO_2 , BET surface area is plotted against carbon content in Fig. 2. It shows a dependence of BET surface area on carbon content for the carbon layers coated on TiO_2 particles, which is common for three carbon precursors employed.

Values of BET surface area observed on carbon-coated TiO_2 are pretty high, reaching $250 m^2/g$, and are much higher than those observed on carbon-coated MgO in previous section. Surface area of TiO_2 powders used was relatively high as $300 m^2/g$ for as-received powders, but decreased to $2 m^2/g$ after $900^\circ C$ without carbon coating. If surface areas of carbon layers on TiO_2 particles were calculated on the

basis of the experimental results in the previous section, they were pretty large values, from 1200 to 3000 m²/g, samples with the smaller carbon content tending to give the higher surface area calculated. However, the assumption that the substrate TiO₂ has very low surface area might not be correct, because carbon coating was known to suppress the sintering of TiO₂ particles. Even though a part of surface area was coming from the substrate TiO₂, the carbon layers formed on TiO₂ particles were concluded to have relatively high surface area. It has to be pointed out that porous structure of substrate ceramics may give certain effect on carbon yield of 900 °C carbonization of precursors and also pore structure of resultant carbon layers.

Higher carbon yield on porous TiO₂ than that on non-porous MgO can be explained as follows; carbonaceous decomposition products of precursors can penetrate into pores in the substrate and carbonization in these limited spaces (in the pores) may lead to higher amount of carbon residues.

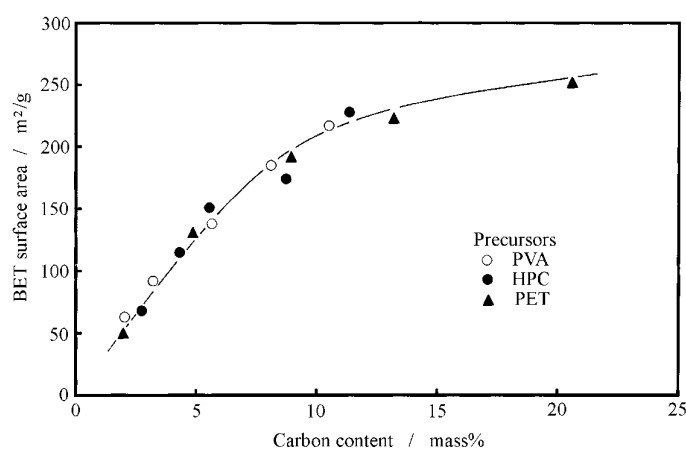


Fig. 2 Dependence of BET surface area of carbon content of carbon-coated TiO₂.

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References

- [1] Inagaki M, Miura H, Konno H. J Europ Ceram Soc 1998; **18**: 1011-15.
- [2] Inagaki M, Hirose Y, Matsunaga T, Tsumura T, Toyoda M. Carbon. 2003; 41: 2619-24
- [3] Tsumura T, Kojitani N, Toyoda M, Inagaki M. J. Mater Chem. 2002; 12: 1391-96.
- [4] Tryba B, Morawski AW, Tsumura T, Inagaki M. Appl. Catal. B: Environ. (in press).
- [5] Tryba B, Morawski AW, Tsumura T, Toyoda M, Inagaki M. Photochem. Biochem. (submitted).